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If a mixture of the two gases is adsorbed then as above the final pressure reached is considerably higher.

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[1] This article is published with the approval of Major General William L. Siebert, Director Chemical Warfare Service, U. S. A.

[2] Gehloff, *Leipzig, Physik, Zs.*, **7**, 1913, (838).

[3] Dewar, *London, Proc. Roy. Soc.*, **74**, 1904, (122).

[4] Bergter, *Leipzig, Ann. Physik*, **37**, 1912, (606).

VARIATIONS, DUE TO HEAT TREATMENT, IN THE RATE OF ADSORPTION OF AIR BY COCOANUT SHELL CHARCOAL[1]

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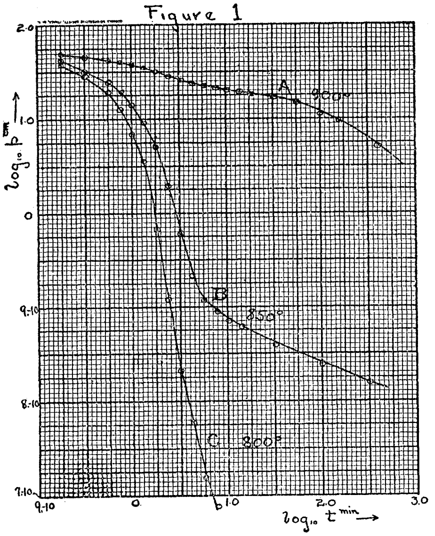
This paper is an abstract of results of experiments most of which were performed prior to January 1918, but the publication of which has been withheld during the war.[1]

If charcoal contained in a bulb of glass or iron is heated to 600°C for about four hours and the gases which are freed pumped off into the low vacuum furnished by a mercury diffusion pump,[2] it is a well known fact that when the charcoal is then subsequently cooled to the temperature of liquid air it possesses a tremendous capacity for adsorbing gas, and will adsorb it at an extremely rapid rate. This adsorption power, however, has been found to be very different with different specimens of charcoal made from the same material, in this case cocoanut shell, and also to be very different when a single sample is used repeatedly. The magnitude of these differences is of no mean order but may be as large as the ratio of 10,000 : 1. It is shown in what follows that the heat treatment of the specimen during carbonization and also during successive 'outgassings' is a decisive factor in the control of the efficiency of the material as an adsorbent.

The experimental method was one of extreme simplicity. The shell was carbonized in an enclosed electric furnace having a vent for escape of gases and vapors. The temperature was indicated on a Leeds Northrup potential point resistance thermometer. The charcoal was then ground up to particles of from 1 to 3 mm. diameter and cleansed from all smaller fragments and dust. A definite weight (25.7 grams in most of the experiments, determined in dry air with which the charcoal was saturated) was sealed up in a tube of iron, quartz or Pyrex glass depending on the temperatures to be subsequently used. From this tube cocks communicated, (1) to the diffusion pump, and (2) to a fixed volume that could be filled with dry air at any desired pressure. This fixed volume included a McLeod gauge and a mercury barometer column so that the pressure in it could be read to within a few per cent over a range of from 100 cm. to 0.00001 cm. A small Geissler tube was in communication with the charcoal bulb for a rapid means of observing the character of the gas content and, qualitatively, the pressure. After outgassing through cock, *1*, this was closed and cock, *2*, opened. The charcoal was thus exposed to a constant volume of 873 cc. initially filled with air at about 90 cm. pressure. This initial pressure was varied slightly as the room temperature varied so that the enclosed mass of air was constant, i.e. 1.2 grams. The air was immediately adsorbed and the rate of fall of the pressure observed as long as it was appreciable.

Results are expressed graphically by plotting the logarithm of the pressure in cm. against the logarithm of the time in minutes elapsing after the cock, *2*, was opened. Figure 1 shows curves for three different samples under identical conditions. *A* was carbonized at 900°C., *B* at 850°C. and *C* at 800°C. They were all outgassed simultaneously for 6 hours at 425°C. and tested in rapid succession on the same apparatus. The enormous difference in rate is obvious in view of the logarithmic scales. The initial pressure of 90 cm. is reduced in 10 minutes to 20 cm., 0.71 cm. and 0.0003 cm. for *A*, *B* and *C* respectively.



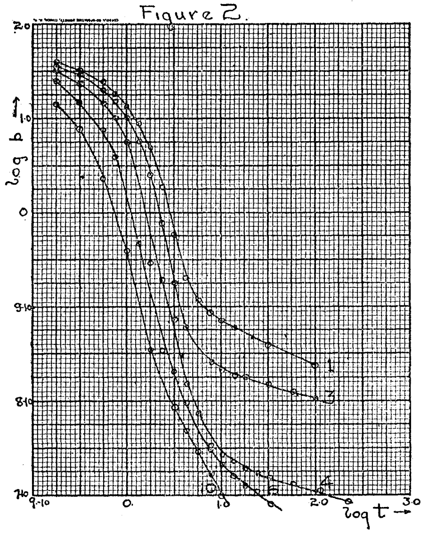


Figure 2 shows the results of successive 'runs' on the same specimen. This specimen was carbonized at 850°C. and the outgassings were all identical at 600° for $4\frac{1}{4}$ hrs. It shows a systematic increase in rate after each run and subsequent outgassing becoming equal after 10 consecutive runs to the former sample shown as *C* in figure 1.

Figure 3 shows an effect which was controlled so as to be the converse of that illustrated in figure 2. It depicts also successive runs on a single specimen, the carbonization of which was for 3 hours at 670°C. The first run shows an extremely active adsorption. Successive outgassings were not now identical but were as indicated below:

First	4.5 hours at 633°C.
Second	0.5 hours at 800°C.
Third	0.5 hours at 850°C.
Fourth	0.5 hours at 875°C.
Fifth	4.0 hours at 640°C.
Sixth	0.7 hours at 905°C.

The first four runs show a cumulative loss of activity as result of high outgassing temperature. In the fifth the activity is in part restored by prolonged outgassing at the lower temperature and in the sixth it is again almost totally destroyed. Quartz tubes are unsuitable for use for the high temperature work because of their devitrification by the hot carbon vapor.

Figure 3.

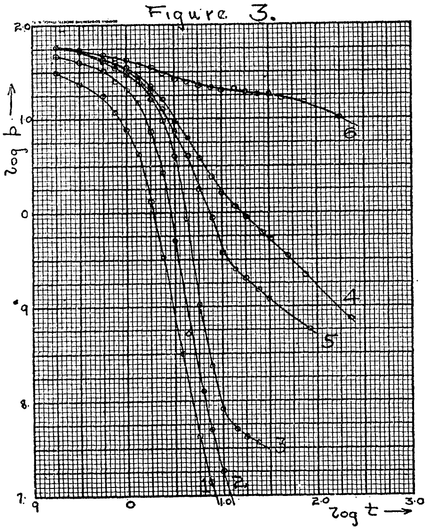


Figure 4.

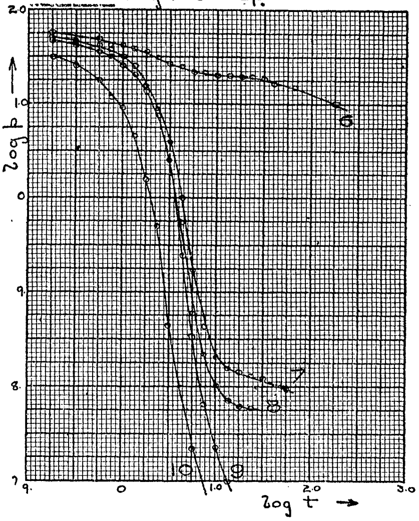


Figure 4, repeating the sixth run shown in the preceding, carried the same sample back to high activity in four subsequent outgassings which were as follows:

Seventh	22.0 hours at 650°C.
Eighth	22.0 hours at 500°C.
Ninth	44.0 hours at 650°C.
Tenth	1.0 hours at 840°C.

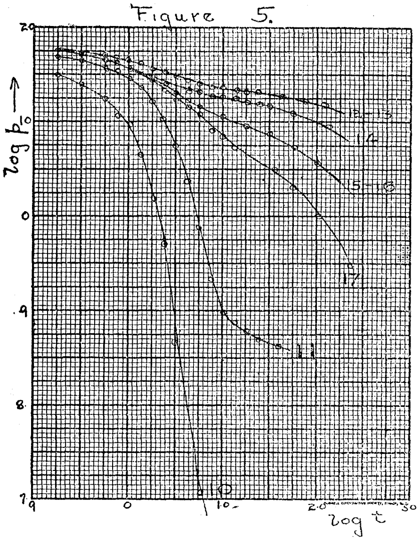
A sluggishness of behavior is apparent after this much use as indicated in the long times necessary to produce a change in quality and also in the failure to respond as before to a temperature higher than 800.

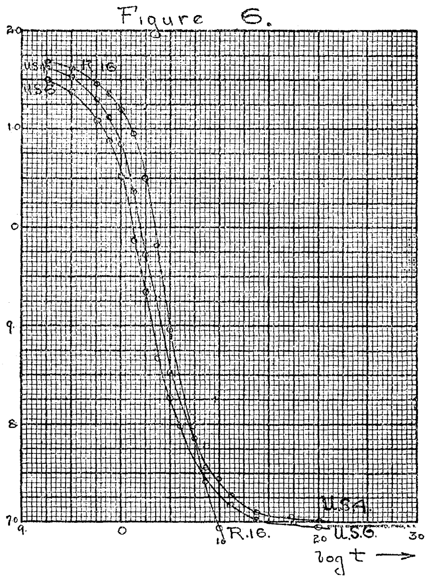
Figure 5 shows continuation of the attempt for the second time to destroy the activity. Repeating curve 10 of the preceding and outgassing

Eleventh	0.5 hours at 950°C.
Twelfth	1.5 hours at 985°C.

the activity is again reduced. Recovery is now as before sluggish and was not carried to completion.

Thirteenth	3.0 hours at 650°C.
Fourteenth	8.0 hours at 625°C.
Fifteenth	12.0 hours at 645°C.
Sixteenth	1.5 hours at 650°C.
Seventeenth	14.0 hours at 650°C.





The characteristic form of the family of curves shown is undoubtedly of generic quality. These curves have been reproduced on a wide variety of samples of cocoanut shell charcoal many times; and when the results are assembled exhibit almost every degree of gradation from a central, closely linear (after the first minute) relationship. Similar experiments on pure gases rather than air are in progress in the hope of simplifying this family of curves somewhat so as to obtain an interpretation expressible in analytic form.

Two hypotheses have been advanced for these phenomena. One ascribes the changes in the sense of increased activity to the gradual distillation out of the material of heavy nonvolatile hydrocarbons, many of which in the form of tars and gums come off during the initial carbonization. The other is based on the conception advanced by Miss Ida Homfray[3] that these phenomena are to be regarded as saturated solutions of a rigid phase, carbon, in a fluid phase, gas. It suggests that repeated solution and subsequent evaporation, here taking the form of adsorption at low temperatures and outgassing at high, produces a gradual modification of the character of the carbon with respect to its fineness of division, something similar to precipitation occurring.

Loss of activity seems difficult to account for on the first hypothesis. It is to be noted that permanent loss of activity can always be produced on any sample by heating to 1200°C. This is usually ascribed to a partial destruction of porosity and has been observed before. Attempts to extract heavy hydrocarbons by the use of the lightest liquid solvents, ligroin alcohol and acetone were inconclusive. Considerable amounts of tarry material were removed, but not by the solvents directly. They distilled out during outgassing after treatment with the solvent. This treatment in all cases causes temporary loss of activity which is renewed in the usual manner with repeated use after low temperature outgassings. Experiments by others however[4] which have shown that activation is possible by other methods than the ones here outlined seems to favor the hydrocarbon hypothesis.

Those other methods for activation of field material for the adsorption of complex vapors have been used in conjunction with the above described process. A comparison of material activated by use and low temperature outgassings alone as herein described, with the most highly activated charcoals produced elsewhere under the conditions of these experiments is given in figure 6. The crossing of the curves may be very significant. The laboratory charcoal, R. 16, is less active initially but ultimately runs to lower values than the field material U. S. 4 and U. S. 6. The differences at either end are not large in comparison with the range of the phenomena discussed above.

Experiments are in progress on saturation values for adsorptions of mixtures of varied proportions. An hypothesis originally advanced by McBain[5] that there is a distinction to be made between surface condensation and interior diffusion is also being subjected to experimental scrutiny with modern materials now at our disposal. Both of these lines of work it is hoped will shed light on the mechanism of the process.

A more detailed account of this work will shortly appear in the Physical Review as a series of papers under the general title of Studies in Charcoal Adsorption.

[1] This article is published with the approval of Major General William L. Siebert, Director Chemical Warfare Service, U. S. A.

[2] Shrader, *Ithaca, N. Y. Physic. Rev.*, 12, 1918, (70).

[3] Homfray, *Liepzig, Zs. Phys. Chem.*, 74, 1910, (139).

[4] Dorsey, *Easton, Pa., J. Ind. Eng. Chem.*, 11, 1919, (284).

[5] McBain, *London, Phil. Mag.*, 18, 1909, (916).